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# Assessment of the Long-term Stability of the Polymer of Intrinsic Microporosity PIM-1 for Hydrogen Storage Applications

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## Abstract

Polymers of intrinsic microporosity, such as PIM-1, advantageously combine high surface areas with good processability, which are attractive properties for hydrogen storage applications. Here we address the lack of data on the long-term mechanical stability and hydrogen uptake capacity of PIM-1 in a study carried out over 400 days. Our results show that most mechanical and surface properties of PIM-1 remain stable over this time. In particular, the mechanical strength and elasticity are maintained, and the surface area remains constant over the course of our observations. In contrast, we detected a small but statistically significant decrease of the hydrogen storage capacity of the material over time, particularly in the first stages of aging. We attribute this phenomenon to the slow rearrangement of the polymer scaffold in the solid state. Taken together, our experiments demonstrate that PIM-1 possesses the long-term stability required for realistic applications in hydrogen storage or in gas separation.

## Keywords

Hydrogen storage

Polymer of intrinsic microporosity

Porous material

Physisorption

Long-term stability

Tensile test

## Introduction

Hydrogen as an energy vector represents a promising alternative to carbon-based fuels, and is expected to contribute significantly to the energy mix of the near future.[1] The storage of hydrogen is one of the hurdles that currently limit applications of hydrogen-powered systems, in particular for mobile applications where available volume and weight are limited. Hydrogen is an appealing fuel owing to its exceptionally high gravimetric energy density and higher heating value of 142 MJ kg<sup>-1</sup>, however its practicality is limited by its very low volumetric density at ambient conditions.[2] As a result, various methods to densify hydrogen have been proposed, in addition to compression or liquefaction, based on the uptake of hydrogen on solid-state supports, via either physisorption or chemisorption.[3] Of relevance to this work, numerous high-surface area physisorbents have been reported over the last decade, which are able to store significant quantities of hydrogen.[4] The most common examples include metal-organic frameworks (MOFs),[5, 6] covalent organic frameworks

(COFs),[7] porous aromatic frameworks (PAFs),[8] activated carbons,[9] hypercrosslinked polymers (HCPs),[10] and microporous polymers.[11-14] Criteria such as affordability, thermal and structural stability and hydrogen uptake capacity are typically used to assess the viability of a material for hydrogen storage applications.[15] In our work, we consider an additional criterion, as we require the developed materials to be processable and flexible. Indeed, when used in high-pressure storage tanks, finely divided powders cause additional technical difficulties as well as potential safety concerns. Materials which are processable and conformable while possessing a sufficient hydrogen uptake capacity are thus advantageous in this context. Among the rare materials combining high surface area and processability, polymers of intrinsic microporosity (PIMs)[11, 16] represent a promising class of compounds. They have been extensively studied,[17] and used to create separation membranes[18-28] and gas storage materials.[12, 19, 29, 30] Our group recently studied the capacity of PIM-1 for hydrogen storage and its mechanical properties,[31, 32] and demonstrated that its relatively limited surface area and hydrogen uptake capacity can be significantly enhanced by addition of high-surface area fillers.[33] An important parameter to consider when evaluating these materials is their long-term behaviour and stability. For example, the ultimate target for durability issued by the U.S. Department of Energy (DoE) mentions 1500 charging/discharging cycles over 15 years.[34] Glassy polymers such as PIM-1 are intrinsically non-equilibrium materials and are known to lose free volume over time, owing to slow rearrangements in the packing of the polymer chains. This physical aging[35] was found to be the primary cause of the well-established decay in permeability of PIM-1 membranes over time.[36] Interestingly, aging of the polymer was found to impact not only its permeability, but also to enhance its selectivity,[37] which is a critical parameter when evaluating the performance of polymer-based membranes. The possibility to “reset” the polymer to its initial state by treatment with alcohols,[38, 39] and the anti-aging effect of porous fillers were also reported.[40] To the best of our knowledge, the work described herein represents the first study on the aging of PIM-1 with regard to properties such as mechanical strength, surface area and hydrogen uptake capacity.

## Experimental

PIM-1 was prepared and characterised according to published procedures,[17, 33] and a polymer with a number-average molecular weight ( $M_n$ ) of 55 000 g mol<sup>-1</sup> and a polydispersity index of 5.1 was obtained. Self-standing PIM-1 films were prepared by casting chloroform solutions (2 wt%) in covered glass Petri dishes (20 cm diameter) to allow slow evaporation over 1-2 days. The films were then recovered, cured in a vacuum oven at 80 °C for 8 hours to remove residual solvents, and stored in a chamber with controlled, constant temperature (20 °C) and relative humidity (50%). Films were taken out of the chamber periodically to perform mechanical and surface analyses.

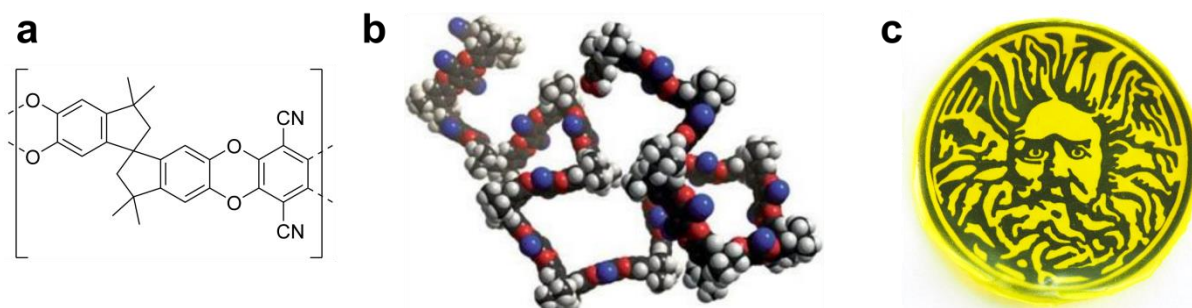
The mechanical properties of the films were determined with static uniaxial tensile tests. Samples were prepared as previously described,[31] following the BS EN ISO 527-3:1996 standard (1/2 of Specimen type 2), and their thickness was measured with a Mitutoyo 227-211 Absolute Digimatic Micrometer with measuring force adjustment and accuracy of  $\pm 0.001$  mm. Static uniaxial tensile tests were carried out on an Instron 3369 instrument equipped with a 50 N static load cell. A quasi-static speed of 2 mm min<sup>-1</sup> was used under room temperature and humidity conditions. Samples with visible imperfections were excluded from the test, and tests where slipping occurred were not taken into consideration.

Surface area measurements were carried out using the BET method on N<sub>2</sub> adsorption isotherms measured at 77 K using a Belsorp II Mini surface analyser (MicroTrac/BELJapan). The surface area of samples was calculated in pressure ranges determined based on

consistency criteria recommended by Rouquerol et al.[41] Low-pressure hydrogen adsorption experiments (up to 120 kPa) were performed using a 3Flex instrument from Micromeritics, and high-pressure hydrogen uptake experiments (up to 10.6 MPa) were carried out using a Sieverts-type volumetric gas dosing analyser (HTP-1) from Hiden Isochema. High-purity hydrogen was used (BIP PLUS grade from Air Products) and the measurements were performed at 77 K. All H<sub>2</sub> isotherms were measured in triplicate on ~100 mg samples. High-pressure hydrogen uptake isotherms were modelled using a methodology developed at the University of Bath, which assumes a two-phase system in the pores in which the density of adsorbate is constant.[42, 43] Fitting the measured excess uptake isotherm affords the total amount of hydrogen present in the material, which comprises adsorbed hydrogen and hydrogen compressed at the centres of the pores. The fitting procedure was performed with Origin Pro software (OriginLab) which uses a Levenberg-Marquardt method of non-linear fitting. All samples were degassed under high vacuum at 80 °C for 15 hours before any N<sub>2</sub> or H<sub>2</sub> adsorption experiment.

## Results and discussion

As critical parameters in our search for porous, processable and conformable materials for hydrogen storage, the mechanical and surface properties of PIM-1 films (Figure 1), as well as their hydrogen uptake capacity were monitored at intervals over 400 days. The films were stored in a chamber with controlled, constant humidity and temperature between measurements (see Experimental).



**Figure 1.** a) Chemical structure of PIM-1; b) Structural model of PIM-1 showing its contorted nature leading to enhanced microporosity (adapted from ref. [16] with permission from The Royal Society of Chemistry); c) Transparent, solvent-cast, 5-cm diameter membrane made of PIM-1 over the logo of the University of Bath.

The ultimate strain and stress measured at the beginning of our evaluation (day 1) showed values falling in the upper range of those indicated in prior reports,[31] *i.e.* an ultimate stress of 45 MPa for a strain to failure of 8.4% (Figure 2a). We observed a slight decrease of the ultimate stress over the first 200 days of aging, after which it slowly increased again over the next 200 days. Although we did not observe a clear trend in ultimate strain, it decreased from 8.4% to 6.9% between day 1 and day 400. We performed statistical analyses based on a two-tailed *t*-test to investigate the significance of the variations between consecutive tests, which showed that the differences in ultimate stress cannot be considered statistically significant ( $p > 0.05$ ). However, the decrease in ultimate strain between fresh (day 1) and aged samples (day 400) can be considered statistically significant. In this case, owing to the large standard deviations of our measurements, the results fall within the error limits, and therefore, the decrease in strain is not substantial. The resulting Young's modulus (which represents the slope of the stress-strain curve in the elastic regime) was also found to remain relatively constant over the 400-day period (Figure 2b), which underlines that the elasticity of the material is conserved upon aging. Variations in results can be attributed to differences in films and samples caused by an arbitrary evaporation process. From these

measurements, we conclude that the key mechanical properties of PIM-1 (tensile strength and elasticity) are maintained over time in a range that makes them suitable for use as liners in hydrogen storage tanks. Indeed, carbon fibres are the constituent of such tanks with the lowest strain to failure (between 0.4 and 1.9%), and PIM-1 is superior to them in that regard.[31]

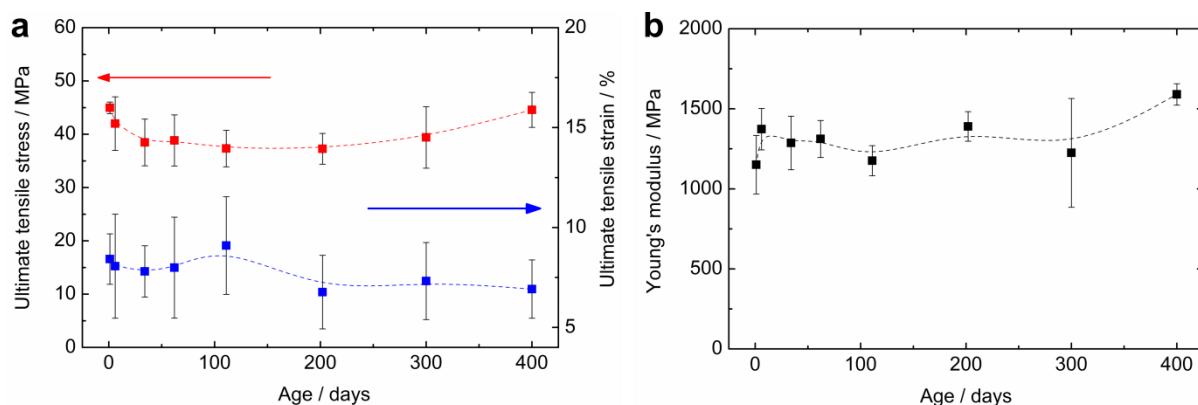


Figure 2. a) Ultimate tensile stress (red) and strain (blue) of PIM-1 films over time; b) Young's modulus of PIM-1 films over time. All measurements were repeated on at least nine independent samples, and error bars represent standard deviations. Dotted lines are provided to guide the eye.

In order to gain insight on the evolution of surface properties of PIM-1 over time, we measured the surface area of samples and their hydrogen uptake properties (Figure 3). The surface areas were determined using the BET model on nitrogen adsorption isotherms measured at 77 K, and were found to be stable over time as no statistically significant evolution was observed during the 400 days of our study. On average, the determined BET surface area was  $761 \text{ m}^2 \text{ g}^{-1}$ , which is within the expected range for thin films made of PIM-1.[17, 33] At a pressure of 100 kPa, the hydrogen uptake of the polymer was similarly found to be constant over time. Within the experimental error of such measurements, the average hydrogen uptake at 100 kPa and 77 K is 0.81 wt%, which is consistent with values reported in prior articles.[31, 33] As low-pressure hydrogen uptake is based almost solely on surface adsorption, a constant hydrogen uptake at 100 kPa and 77 K is consistent with a constant surface area.

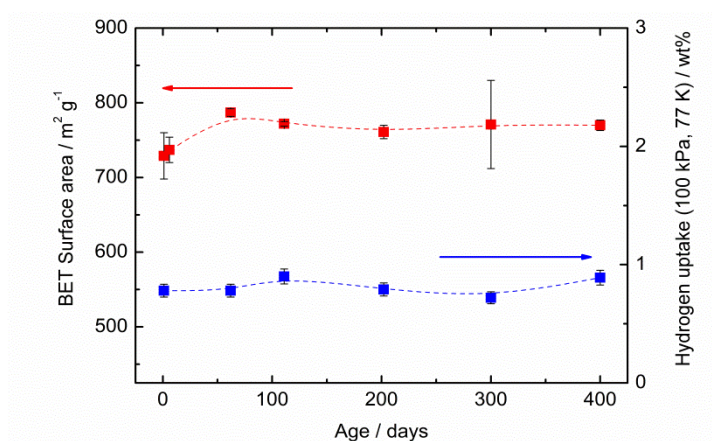


Figure 3. BET surface area (red) and hydrogen uptake (blue, measured at 100 kPa and 77 K) of PIM-1 films over time. Error bars on the BET surface areas represent the error associated with the linear regression analysis part of the BET method, whereas error bars on hydrogen uptakes represent the average variation we typically observed on running independent measurements (7%). Dotted lines are provided to guide the eye.



To assess the potential of PIM-1 for hydrogen storage under realistic conditions, we performed hydrogen uptake experiments at higher pressures, up to 10 MPa. Owing to the complexity of the measurements and the instrument time required, we limited our high-pressure uptake measurements to days 1, 111 and 400, as shown in Figure 4. Within the available data, we observe a marked decrease in total hydrogen uptake between days 1 and 111, as the total hydrogen uptake estimated at 10 MPa decreased from 2.60 wt% to 2.15 wt% in that time interval. The hydrogen uptake then further decreased between day 111 and day 400 (at which point it was determined to be 1.90 wt% at 10 MPa), albeit at a reduced rate. We hypothesise the loss of capacity at high pressures stems from the rearrangement of the polymer scaffold over time. Two structural changes can result from such rearrangements: a) Firstly, a collapse of the largest pores, leading to a smaller available free volume inside the material, has been observed as a consequence of polymer aging.[36] As a result, once the surface is saturated with adsorbed hydrogen, less space is available to compress additional gas at the centre of the pores, which in turn reduces the uptake at high pressures. b) Secondly, age-related collapse of ultramicropores ( $< 0.7$  nm), which are crucial for hydrogen adsorption,[5] can also translate into a decreased total uptake. Either phenomena would not necessarily induce a marked change in surface areas determined with nitrogen adsorption, and therefore would not contradict the findings shown in Figure 3. The collapse of large pores would translate in a reduced free volume rather than a reduced surface area, whereas ultramicropores are notoriously difficult to probe via  $N_2$  adsorption at 77 K,[44] and might be overlooked in surface areas determinations. Hydrogen uptake at low pressure (up to 100 kPa, Figure 3) would not be impacted by such structural changes either, as long as enough surface area remains available for hydrogen adsorption. Importantly, while these structural rearrangements influence the microscopic structure of the polymer, they do not translate into significant changes in the mechanical properties of the bulk material, as reported in Figure 2. Even if the hydrogen storage capacity stabilises over time, its gradual decrease represents an important parameter to take into account when evaluating or using PIM-1 based materials for hydrogen storage. It also provides a strong incentive to add porous fillers (e.g. PAF-1) to PIM-1-based membranes, which not only enhance their hydrogen storage capacity,[33] but have been demonstrated to provide an additional long-term structural stability.[22, 40]

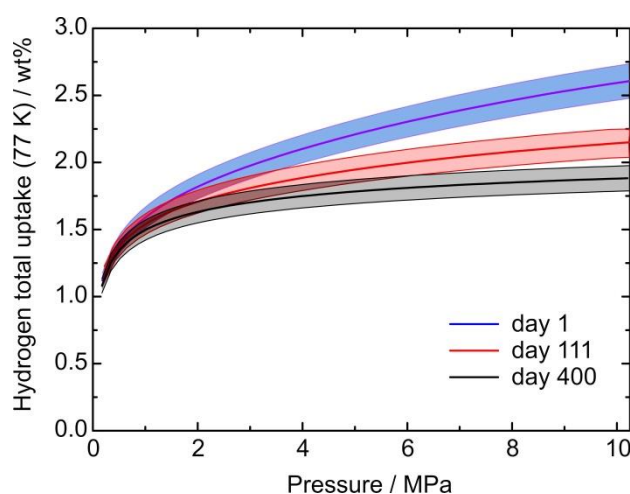


Figure 4. High-pressure hydrogen uptake of PIM-1 films at 77 K after 1, 111 and 400 days. The total uptakes are calculated based on modelling of experimentally determined excess uptakes (see references [33] and [42] for details). The shaded areas represent the 5% uncertainties resulting from experimental variations and modelling procedures.

## Conclusions

This study reports the first long-term evaluation of the mechanical properties and hydrogen uptake capacity of PIM-1, monitored over 400 days. We observed that the mechanical properties (ultimate tensile stress and strain, elasticity) are maintained over that period of time, confirming PIM-1 as an attractive and processable material. The surface area of PIM-1 films was found to remain constant over time, which is a critical parameter for hydrogen storage via surface adsorption. However, the hydrogen uptake under high pressure was found to slowly decrease over time, which we attribute to rearranging of the polymer scaffold which limits the available free volume inside the polymer. These are important results as long-term stability is a crucial parameter if PIM-1 based materials are to be used in applications such as mobile hydrogen storage or gas separation membranes. Our observations confirm the potential of PIM-1 for these applications based on its long-term mechanical and structural stability, and allow us to reiterate the advantageous use of high surface area fillers as means to enhance the long-term internal stability of the polymer microporous network.

## Acknowledgement

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